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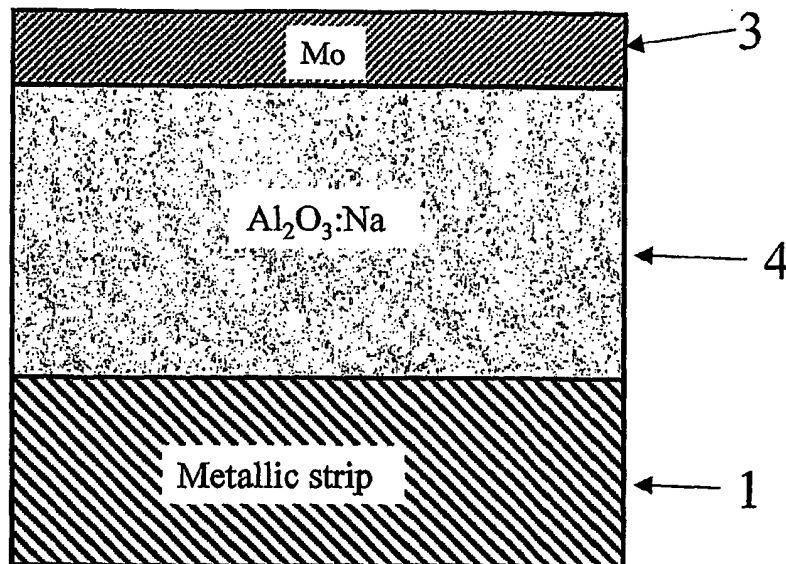
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(54) Title: NEW METAL STRIP PRODUCT



(57) Abstract: A coated steel product comprises a metallic strip material which has a coating comprising an electrically insulating layer doped with sodium. The thermal expansion coefficient of said metallic strip material is less than  $12 \cdot 10^{-6} \text{ K}^{-1}$  in the temperature range 0-600°C. Said product may be coated with an electrically conducting layer of molybdenum. The coated steel product is useful as a substrate for flexible Cu (In, Ga) Se<sub>2</sub> (CIGS) solar cells.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**NEW METAL STRIP PRODUCT**

The present invention relates generally to a coated metallic substrate material suitable for manufacturing of flexible solar cells and a method of manufacturing of a metal oxide coated metal strip product in a roll-to-roll process. This is achieved by coating a metallic strip with an electrically insulating inner layer in accordance with claim 1 and also optionally with an electrically conducting surface layer.

**Background of the Invention**

The most common substrate material used today by manufacturers of thin film  $\text{Cu(In,Ga)Se}_2$  (abbreviated CIGS) solar cells is sodalime glass. Two examples of solar cells with glass substrates are DE-A-100 24 882 and US-A-5 994 163. A positive effect by the use of sodalime glass is an increased efficiency of the solar cell, due to the diffusion of an alkali metal (primarily sodium) from the glass into the CIGS layer. This fact is known from, e.g., the Thesis by Karin Granath (1999): The Influence of Na on the Growth of  $\text{Cu(In,Ga)Se}_2$  Layers for Thin Film Solar Cells, Acta Universitatis Upsaliensis, Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 491, Uppsala ISBN 91-554-4591-8, hereby incorporated into the present disclosure by this reference. However, the batch-like production of CIGS on glass substrates is expensive and, therefore, it is an advantage to use roll-to-roll production of solar cells, which lowers the production cost. Moreover, there are several technical advantages with flexible solar cells produced by a roll-to-roll process, for instance, the flexible solar cells can be folded or rolled into compact

packages and they may be used for making light weight solar cells, which is desirable for portable, spatial and military applications.

Several materials have been tested as substrate materials for flexible CIGS solar cells, including polymers such as polyimide and metals such as molybdenum, aluminium and titanium foils, bearing in mind that they all have to fulfil certain criteria. Thus, the substrate material should be thermally resistant in order to withstand further process steps in the production of thin film flexible CIGS solar cells, and this may include heat treatments at temperatures up to 600°C under corrosive atmosphere. The flexible metallic substrate should be insulated from the electrical back contact if CIGS modules with integrated series connections are to be produced. Therefore, it is essential that the thermal expansion coefficient (TEC) of the substrate material should be as close as possible to the TEC of the electrical insulating metal oxide layer(s) to avoid thermal cracking or spallation of the insulating metal oxide layer.

Common conventional substrate materials for the production of CIGS solar cells are:

- Using sodalime glass substrates in batch-like processes;
- Depositing a molybdenum back contact material directly onto the metal strip that constitutes the substrate;
- Depositing insulating silicon oxide ( $\text{SiO}_x$  or  $\text{SiO}_2$ ) layers onto metal strips in batch type deposition processes.

One example of a known solar cells are disclosed in Thin Solid Films 403-404 (2002) 384-389 by K. Herz et al.: "Dielectric barriers for flexible CIGS solar modules", hereby incorporated into the present disclosure by this reference. According to this article, excellent electrical insulation for the preparation of CIGS solar modules was

obtained on metal substrates by using  $\text{SiO}_x$  and/or  $\text{Al}_2\text{O}_3$  barrier layers. However, due to the lack of sodium, the voltage produced by the solar cell was inferior.

5 A further example of known solar cells making use of stainless steel substrates are disclosed in Solar Energy Materials & Solar Cells 75 (2003) 65-71 by Takuya Satoh et al.: "Cu(In,Ga)Se<sub>2</sub> solar cells on stainless steel substrates covered with insulating layers", hereby incorporated into the present disclosure by this reference.  
10 However, according to this article, the CIGS solar cells on the stainless steel decreased open-circuit voltage compared with that on the soda-lime glass substrates.

Moreover, in WO 03/007386 (hereby incorporated into the present disclosure by this reference) a thin-film solar  
15 cell is described. It comprises a flexible metallic substrate having a first surface and a second surface. A back metal contact layer is deposited on the first surface of the flexible metallic substrate. A semiconductor absorber layer is deposited on the back metal contact. A  
20 photoactive film deposited on the semiconductor absorber layer forms a heterojunction structure and a grid contact deposited on the heterojunction structure. The flexible metal substrate can be constructed of either aluminum or stainless steel. Furthermore, a method of constructing a  
25 solar cell is disclosed. This method comprises providing an aluminum substrate, depositing a semiconductor absorber layer on the aluminum substrate, and insulating the aluminum substrate from the semiconductor absorber layer to inhibit reaction between the aluminum substrate and the  
30 semiconductor absorber layer.

Although this known solar cell works satisfactorily, it does not attain the open-voltage level of a solar cell with a soda-lime glass substrate because of the lack of sodium doping.

Thus, all these conventional methods have their respective disadvantages. All processes based on batch-type production will always increase the cost and it is therefore essential that the production will be on a roll-to-roll process to decrease the cost.

Hence, when using sodalime glass, it is impossible to produce flexible CIGS, and the batch-type process is expensive. Further, the deposition of Mo back contact directly onto the flexible metal strip substrate will limit the production of CIGS modules with integrated series connections. Furthermore, the  $\text{SiO}_x$  or  $\text{SiO}_2$  insulating layers have a too low TEC, which may lead to the formation of cracks and pinholes during the following process steps. Moreover, by not adding an alkali metal in the  $\text{SiO}_2$  layer, it (primarily sodium) has to be added in a later production step if higher efficiency CIGS is to be produced. The addition of one or more process steps in a production line is always associated with extra costs.

It is therefore a primary object of the present invention to provide a flexible and light metallic substrate for solar cell production with a thermal expansion coefficient as similar as possible to the insulating metal oxide layer(s).

Yet another object of the present invention is to provide a flexible substrate for solar cells that is inexpensive and which may be produced in a continuous roll-to-roll process.

Still another object of the present invention is to make possible the production of flexible solar cells with increased efficiency as to the voltage attained.

These and other objects have been attained in a surprising manner by creating a coated steel product with the features according to the characterizing clause of claim 1. Further preferred embodiments are defined in the dependent claims.

**Brief Description of the Invention**

Thus, the above objects and further advantages are  
5 achieved by applying a thin continuous, uniform,  
electrically insulating layer of a metal oxide, such as  
aluminum oxide, on the top of a metal strip serving as  
substrate. To the insulating metal oxide a small amount of  
an alkali metal is added to increase the efficiency of the  
10 solar cell. The metal oxide layer should be smooth and  
dense in order to avoid any pinholes, which may otherwise  
function as pathways for electrical conduction when the  
material is further processed. If so desired, and in order  
to ensure safe electrical insulation from the metal strip  
15 substrate, multi-layers (ML) of metal oxides can be  
deposited. The advantage of an ML structure is that it will  
exclude any pinholes or conducting pathways through the  
insulating oxide layer. Furthermore, by depositing a  
continuous uniform dense metal oxide layer on top of the  
20 metallic substrate, it is easier to control the insulating  
properties as well as the thickness of the metal oxide  
layer, compared to for instance anodized oxide layers on  
metallic strips. Moreover, the metal oxide layer will also  
have an enhanced adhesion to the substrate, in comparison  
25 with thermally grown oxide layers. The added alkali metal  
(primarily sodium) will diffuse into the CIGS layer during  
the further process steps in the CIGS production. Further,  
if so required, on top of said metal oxide layer, there may  
then be deposited a molybdenum layer, this for obtaining a  
30 back electrical contact for the production of a thin film  
flexible solar cell.

When several layers of metal oxide(s) are deposited,  
these layers may be of the same metal oxide or of different  
metal oxides.

### Brief Description of the Drawings

Figure 1 shows a schematic cross-section of a first embodiment of the present invention.

Figure 2 shows a schematic cross-section of a second embodiment of the present invention.

Figure 3 shows schematic cross-sections of two further embodiments of the present invention.

Figure 4 shows schematically a production line for the manufacturing of a coated metal strip material according to the invention.

### Detailed Description of the Invention

#### The Metal Strip to be coated

One of the key issues of the underlying metallic strip is that it should have a low thermal expansion coefficient (TEC) in order to avoid spallation or cracking of the deposited metal oxide layers. Therefore, it is desirable that the TEC of the metallic strip be lower than  $12 \cdot 10^{-6} \text{ K}^{-1}$  in the temperature range of 0 to 600°C. This will include materials such as ferritic chromium steels, titanium and some nickel alloys. It is also preferred that the material in the metal strip be sufficiently corrosion-resistant to withstand the environment in which the solar cell will work. The physical shape of the metal is in a strip or foil whose thickness should be in the range of 5 to 200  $\mu\text{m}$ , preferably 10 to 100  $\mu\text{m}$ . Another important parameter is the surface roughness of the metal strip, which should be as smooth as possible; a Ra value of less than 0,2  $\mu\text{m}$  is suitable, preferably less than 0,1  $\mu\text{m}$ .

#### The Insulating Oxide Layer

The electrically insulating oxide layers should adhere well to the metallic strip, in order to ensure highest



possible flexibility of the solar cell. This is achieved by careful pre-treatment of the metal strip prior to the coating, first by cleaning it in a proper way to remove oil residues, etc., which may affect the efficiency of the coating process, and the adhesion and quality of the coating. Thereafter, the metal strip is treated by means of an in-line ion assisted etching process. Moreover, the oxide layer should also be a good electrical insulator in order to avoid any electrical connection between the metallic strip and the molybdenum back contact. This can be achieved by depositing dense and smooth oxide layers to bring about better insulating properties, it being repeated that multi-layered structures may also be deposited. The number of individual oxide layers in a multi-layered structure can be 10 or less. As mentioned above, a multi-layered oxide structure will terminate any pinholes or electrical pathways through the overall metal oxide layer and ensure good electrical insulation of the metallic strip. This fact is illustrated in Figure 3, in which the pinholes are terminated by the adjacent oxide layers. When there are more than one insulating metal oxide layer, then the thickness of each individual oxide layer may be between 10 nm and up to 2  $\mu\text{m}$ , preferably between 0,1 and 1,5  $\mu\text{m}$ . The total thickness of the overall metal oxide layer, both in the case of a single mono layer and multi layers (2 to 10 layers), may be up to 20  $\mu\text{m}$ , preferably 1 to 5  $\mu\text{m}$ .

The chemical composition of the oxide layer could be any dielectric oxide such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{HfO}_2$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  or mixtures of these oxides, preferably  $\text{TiO}_2$  and/or  $\text{Al}_2\text{O}_3$ , most preferably  $\text{Al}_2\text{O}_3$ , although other oxide layers are feasible, both stoichiometric and non-stoichiometric ones.

Furthermore, when the metal oxide coating consists of a plurality of layers (multi-layer), then each individual layer may be of the same metal oxide, or of different metal

oxides. An individual layer may also consist of a mixture of metal oxides.

Moreover, according to the present invention, the oxide layer is doped with an amount of an alkali metal, suitably lithium, sodium or potassium, preferably sodium. The alkali metal concentration in the deposited oxide layer should be between 0,01 and 10% (by weight), preferably 0,1 and 6%, and most preferably 0,2-4%, in order to improve the efficiency of the CIGS solar cell by Na diffusion through the back contact layer in a way similar to the one observed for CIGS deposited on sodalime glass. It is indeed surprising for the skilled man, that the alkali metal in the alkali metal doped oxide layer manages to penetrate through the back contact layer and in a decisive manner influence the performance of the CIGS layer.

When sodium is used, the Na source can be any sodium-containing compound and the Na compound is preferably mixed with the oxide source material prior to the deposition, or the Na can be independently added to the oxide coating in a separate process step. The concentration of Na in the oxide source should be the ones mentioned above. The following Na compounds are useful as Na sources for the oxide layer: Na, Na<sub>2</sub>O, NaOH, NaF, NaCl, NaI, Na<sub>2</sub>S, Na<sub>2</sub>Se, NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, just to list a few.

According to one embodiment of the present invention, when a plurality of metal oxide layers are deposited on the substrate, only the most distal layer, or possibly the two most distal layers, is/are doped with an alkali metal. The reason is of course that mainly this layer or these layers contribute to the diffusion of alkali metal into and past the molybdenum layer and into the CIGS layer in a solar cell.

### Description of the Back Contact Layer

Depending upon further processing steps, and on the specific conditions dictated by the individual client, a top layer consisting substantially of molybdenum is applied on top of the oxide layer. This top layer should be dense and adhere well to the underlying, previously deposited oxide layer, while simultaneously allowing the penetration of the alkali metal(s). The thickness of the molybdenum top layer should be 0,01-5,0  $\mu\text{m}$ , preferably 0,1-2,0  $\mu\text{m}$ , most preferably around 0,5  $\mu\text{m}$ .

### Description of Coating Method

Advantageously, the coating method is integrated in a roll-to-roll strip production line. In this roll-to-roll production line, the first production step is an ion-assisted etching of the metallic strip surface, in order to achieve good adhesion of the adjacent insulating oxide layer. The insulating oxide layer is deposited by means of electron beam evaporation (EB) in a roll-to-roll process. This process is well known for the skilled man and is, e.g., comprehensively described in the book Electron Beam Technology by Siegfried Schiller, Ullrich Heisig and Siegfried Panzer, Verlag Technik GmbH Berlin 1995, ISBN 3-341-01153-6, hereby incorporated into the present disclosure by this reference.

The insulating oxide layer may be either a single or mono layer, or a plurality of layers, so called multi layers. While the mono layer usually works satisfactorily, the multi-layer embodiment gives more safety as to cracks and pinholes. The formation of multi-layers can be achieved by integrating several EB deposition chambers in-line (see Figure 4), or by running the strip several times through the same EB deposition chamber. If a stoichiometric oxide is desired, then the deposition of oxides should be made under reduced pressure with a partial pressure of oxygen as

reactive gas in the chamber. In such a production line, the last chamber should be the EB chamber for the deposition of the molybdenum for the back contact layer. The deposition of Mo should be done under reduced atmosphere at a maximum  
5 pressure of  $1 \cdot 10^{-2}$  mbar.

#### Preferred Embodiment of the Invention

Firstly, the substrate materials are produced by ordinary metallurgical steelmaking to a chemical  
10 composition as described above. They are then hot rolled down to an intermediate size, and thereafter cold-rolled in several steps with a number of recrystallization steps between said rolling steps, until a final thickness of about 0,042 mm and a width of a maximum of 1000 mm. The  
15 surface of the substrate material is then cleaned in a proper way to remove all oil residuals from the rolling.

In Figure 1 a typical cross section of a flexible metallic substrate for the production of thin film CIGS solar cell is illustrated. The substrate material is a  
20 flexible metal strip (1), which can consist of stainless steel, or any other metal or alloy which has a TEC lower than  $12 \times 10^{-6} \text{ K}^{-1}$ , in the temperature range 0-600 °C. The surface roughness of the metallic strip should be kept as low as possible. The thickness of the metallic strip should  
25 be in the range of 5 - 200  $\mu\text{m}$ , preferably 10-100  $\mu\text{m}$  to ensure good flexibility.

On top of the surface of the metallic strip substrate (1), a single layered alkali metal (in this case sodium) doped aluminum oxide (4) may be deposited in a roll-to-roll  
30 EB process, directly on top of the flexible metal strip as illustrated in Figure 2. On top of the electrically insulated single layered alkali metal doped aluminum oxide, also a molybdenum layer can be deposited by means of electron beam deposition in a roll-to-roll process.

As an alternative to the single or mono layer (4) according to Figure 2, an electrically insulating aluminum oxide multi-layer structure (2) may be deposited, also by EB deposition in a roll-to-roll process. The aluminum oxide multi-layer structure should be well adherent to the metal strip as well as dense and smooth.

The deposited aluminum oxide is doped with a small amount of alkali metal, preferably sodium. To create a back contact for the CIGS solar cell, a molybdenum layer (3) may be deposited on top of the electrically insulated metallic strip. The molybdenum layer should be dense and well adherent to the metal oxide coating to avoid cracking or spallation. Furthermore, the molybdenum layer should have a thickness between 0,1 - 5  $\mu\text{m}$ , preferably 0,4-2  $\mu\text{m}$ .

Another variation to the two above-mentioned examples is that no molybdenum back contact layer is deposited on top of the electrically insulating aluminum oxide multi-layer structure (2) or the electrically insulating aluminum oxide single layer (4) deposited by EB deposition in the roll-to-roll process. This is illustrated in Figure 3. In the figure the benefit of a multi-layer metal oxide structure is illustrated by the termination of any pinholes (5) and/or electrical pathways (5) through the metal oxide multi-layers.

The roll-to-roll electron beam evaporation process is illustrated in Figure 4. The first part of such a production line is the uncoiler (6) within a vacuum chamber (7), then the in-line ion assisted etching chamber (8), followed by a series of EB evaporation chambers (9), the number of EB evaporation chambers needed can vary from 1 up to 10 chambers, this to achieve the wanted multi-layered metal oxide structure. All the metal oxide EB evaporation chambers (9) are equipped with EB guns (10) and water cold copper crucibles (11) for the evaporation. The following

chamber is a separate chamber (12) for the EB evaporation of molybdenum top layer, this chamber is also equipped with an EB gun (13) and a crucible (14) for the molybdenum melt. The need for a separate EB evaporation chamber for the

5 molybdenum can be excluded if only metal oxide coated strips are to be produced. After this chamber comes the exit vacuum chamber (15) and the recoiler (16) for the coated strip material, the recoiler being located within vacuum chamber (15). The vacuum chambers 7 and 15 may also

10 be replaced by an entrance vacuum lock system and an exit vacuum lock system, respectively. In the latter case, the uncoiler 6 and the coiler 16 are placed in the open air.

CLAIMS

1. A coated steel product comprising a metallic strip material, **characterized in that** said strip has a coating  
5 comprising an electrically insulating layer doped with an alkali metal or a mixture of alkali metals, the thermal expansion coefficient of said metallic strip material being less than  $12 \cdot 10^{-6} \text{ K}^{-1}$  in the temperature range 0-600°C, the electrically insulating layer comprises at least one oxide  
10 layer and the oxide layer consists essentially of any of the following dielectric oxides:  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{HfO}_2$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  or mixtures of these oxides, preferably  $\text{Al}_2\text{O}_3$  and/or  $\text{TiO}_2$ .
2. Coated steel product according to claim 1, **characterized**  
15 **in that** the metallic strip material has a thickness of 5 to 200  $\mu\text{m}$ , preferably 10 to 100  $\mu\text{m}$ .
3. Coated steel product according to claims 1 or 2, **characterized in that** the electrically insulating layer has a multi-layer constitution of 2 to 10 layers, to ensure  
20 efficient electrical insulation.
4. Coated steel product according to claim 3, **characterized in that** each individual oxide layer has a thickness of between 0,01 and 2  $\mu\text{m}$ , preferably between 0,1 and 1,5  $\mu\text{m}$ .
5. Coated steel product according to claim 1 or 4,  
25 **characterized in that** only the layer, or the two layers, most distal from the metallic strip substrate is/are doped with alkali metal(s).
6. Coated steel product according to any of the previous, **characterized in that** the total thickness of the oxide  
30 coating may be up to 20  $\mu\text{m}$ , preferably 1 to 5  $\mu\text{m}$ .
7. Coated steel product according to any of the previous claims, **characterized in that** the electrically insulating layer is coated by a conducting layer, preferably mainly made of molybdenum.

8. Coated steel product according to claim 7, **characterized in that** the molybdenum layer has a thickness of between 0,01 and 5  $\mu\text{m}$ , preferably 0,1 and 2  $\mu\text{m}$ .
9. Coated steel product according to any of the previous  
5 claims, **characterized in that** the alkali metal is either Li, Na or K, or mixtures thereof, preferably Na.
10. Coated steel product according to claim 3 or 4,  
**characterized in that** the individual layers in the multi-layer structure are either made of the same metal oxide or  
10 of different metal oxides and that each individual layer is made of one metal oxide or of a mixture of two or more metal oxides.
11. Coated steel product according to any of the previous claims, **characterized in that** it is suitable as a substrate  
15 material for the production of flexible  $\text{Cu(In,Ga)Se}_2$  (CIGS) solar cells.
12. Method for producing a coated steel product according to any of claims 1-11, **characterized in that** the electrically insulating layer(s) and the electrically  
20 conducting layer(s) are all deposited in a roll-to-roll electronic beam evaporation process.
13. A flexible  $\text{Cu(In,Ga)Se}_2$  (CIGS) solar cell **characterized in that** it comprises a coated steel product according to any of claims 1-11.



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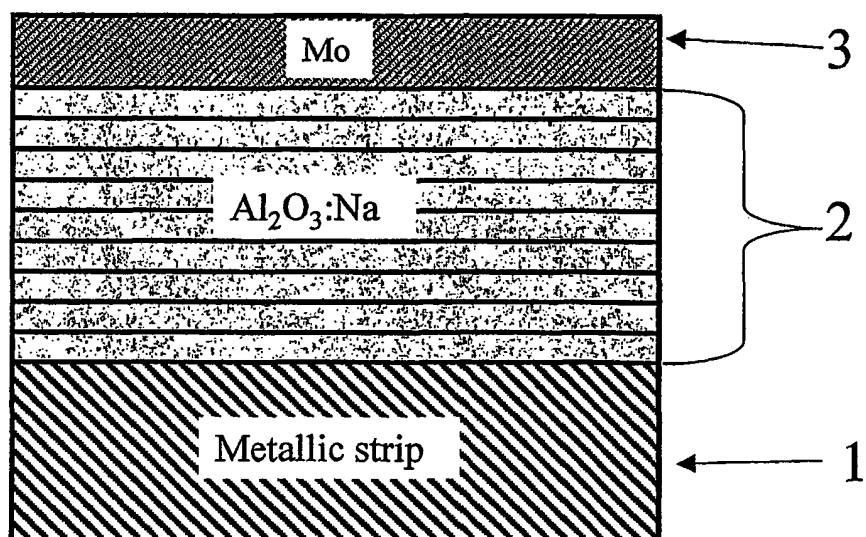


Fig. 1

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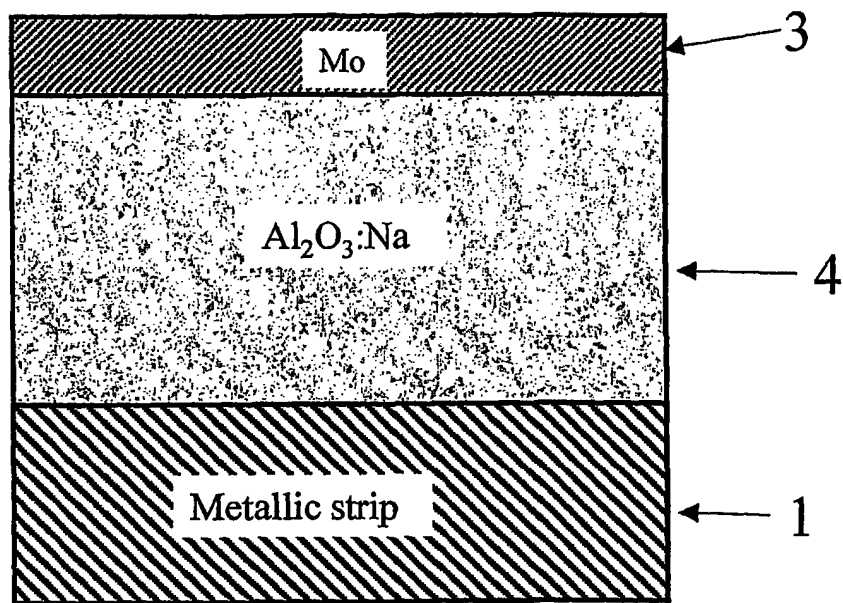


Fig. 2

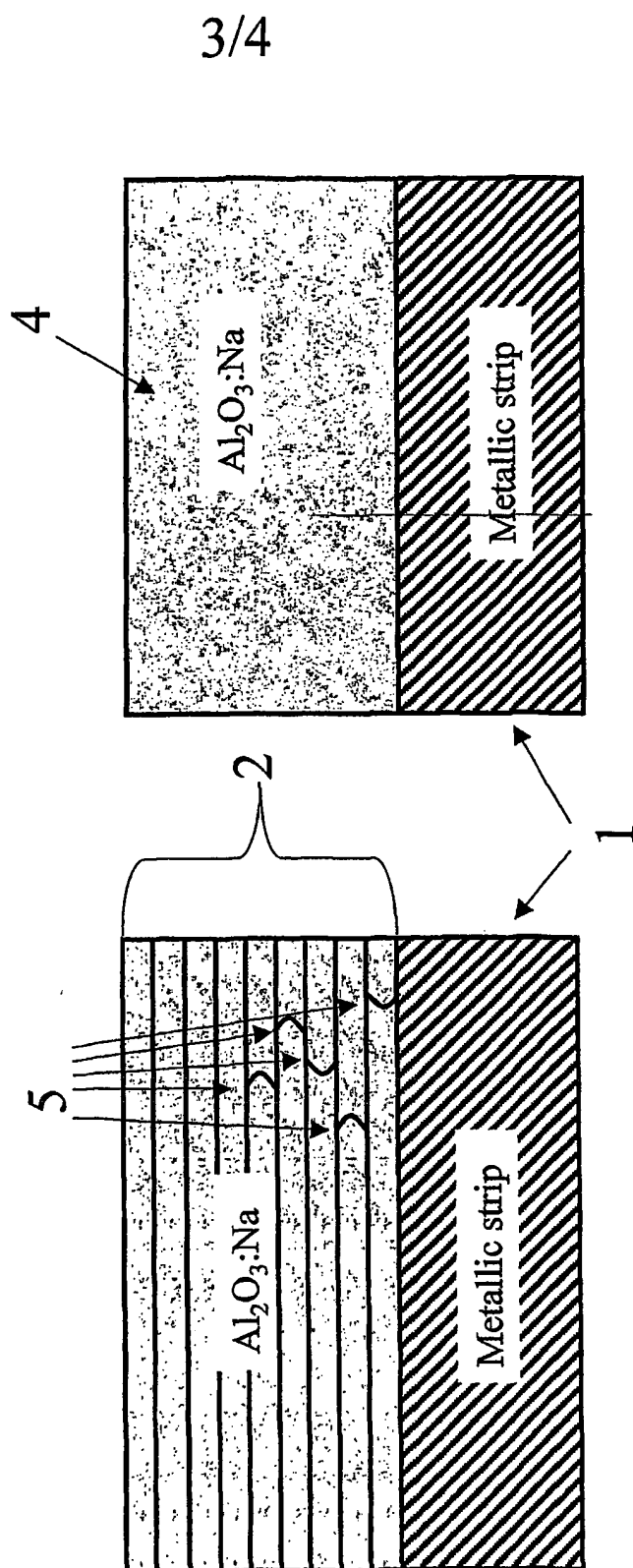


Fig. 3

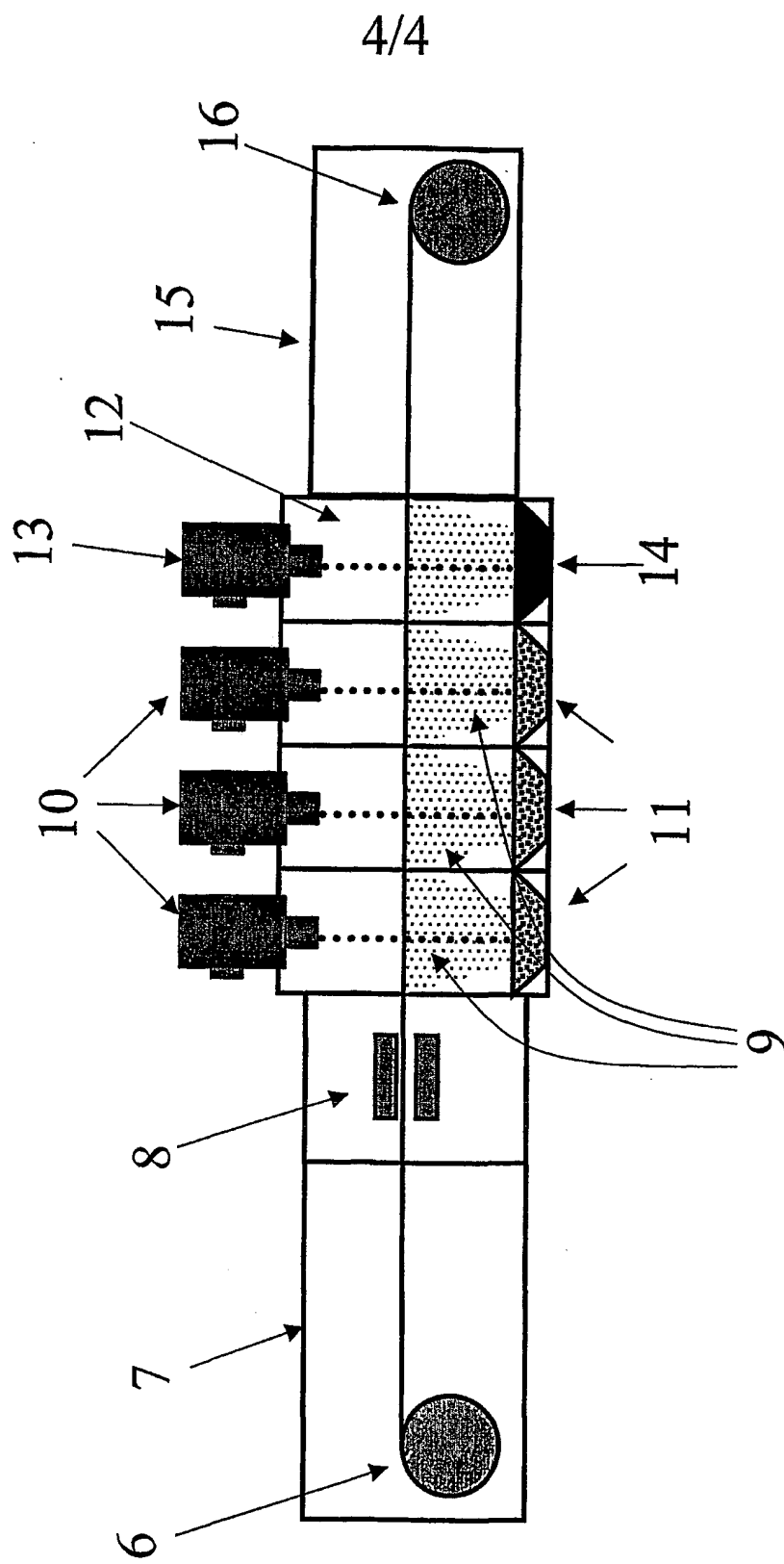


Fig. 4

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 2004/001173

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: H01L 31/02, H01L 31/032

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL, PAJ, IEEE, ELSEVIER

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | K. Herz, et al., "Diffusion barriers for CIGS solar cells on metallic substrates", Thin Solid Films Volumes 431-432, 1 May 2003, Pages 392-397, Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW), Stuttgart, Germany<br>--   | 1-13                  |
| A         | Karin Granath, Marika Bodegård and Lars Stolt, "The effect of NaF on Cu(In, Ga)Se <sub>2</sub> thin film solar cells", Solar Energy Materials and Solar Cells, Volume 60, Issue 3, 31 January 2000, Pages 279-293, Department of Material Science, Ångström Solar Center, Uppsala University, Solid State Electronics, Uppsala, Sweden<br>-- | 1-13                  |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

\* Special categories of cited documents:

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## INTERNATIONAL SEARCH REPORT

International application No.

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|-----------|---|-----------------------|
| A         | <p>Takuya Satoh et al., "Cu(In,Ga)Se<sub>2</sub> solar cells on stainless steel substrates covered with insulating layers", Solar Energy Materials and Solar Cells, Volume 75, Issues 1-2, January 2003, Pages 65-71<br/>Living Environment Development Center, Matsushita Electric Industrial Co., Ltd., Kyoto, Japan</p> <p>--</p>  | 1-13                  |
| A         | <p>K. Herz et al., "Dielectric barriers for flexible CIGS solar modules", Proceedings of Symposium P on Thin Film Materials for Photovoltaics, Thin Solid Films, Volumes 403-404, 1 February 2002, Pages 384-389, Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW), Stuttgart, Germany, Institut für Plasmaforschung (IPF) der Universität Stuttgart, Stuttgart, Germany</p> <p>--</p>            | 1-13                  |
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